REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
May 31, 2003

3. REPORT TYPE AND DATES COVERED
Final Report
16 August 1999 to May 15 2003

4. TITLE AND SUBTITLE
A Novel Approach to Large Electrostriction in Ferroelectrics

5. FUNDING NUMBERS
DAAD19-99-1-0319

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8. PERFORMING ORGANIZATION REPORT NUMBER
4

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
40191.3-EG

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Ferroelectric materials are currently used in a variety of sensor and actuator applications. Conventional materials offer a high frequency, linear response with useful strains of up to 0.1%. Additional applications can be imagined for actuators that generate a greater degree of strain. The current investigation is aimed at offering increased actuator performance over conventional materials. In addition, the study offers insight into the underlying principles of behavior of those materials currently in use. Experimental studies of large strain actuation has been carried out using a single crystal in a novel configuration using Barium Titanate and Lead Titanate. Strains of about 0.9% have been demonstrated in Barium Titanate and about 2% in Lead Titanate. Theoretical studies have explored the possibility of extending this idea to polycrystals and to the ferroelectric/antiferroelectric phase transformation.

14. SUBJECT TERMS
Solid Mechanics; ferroelectric materials; anti-ferroelectric materials;

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

20031114 051

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Mechanics of Large Electrostriction in Ferroelectrics
ARO Grant # DAAD19-99-1-0319
Final Report

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(1) List of Manuscripts

E. Burcsu, G. Ravichandran, K. Bhattacharya, "Large strain electrostrictive actuation in barium titanate" *Applied Physics Letters.* 77: (11) 1698-1700, Sept. 11, 2000.

E. Burcsu, G. Ravichandran, K. Bhattacharya, "Mechanics of large electrostriction in ferroelectrics", In *Proc. SPIE Vol. 3992, Smart Structures and Materials 2000: Active Materials: Behavior and Mechanics* (Ed. C.S. Lynch), SPIE (Mar. 5-8, 2000). pp 296-304.

E. Burcsu, G. Ravichandran, K. Bhattacharya, "Electro-mechanical Behavior of 90-degree Domain Motion in Barium Titanate Single Crystals", In *Proc. SPIE Vol. 4333, Smart Structures and Materials 2001: Active Materials: Behavior and Mechanics* (Ed. C.S. Lynch) (Mar. 4-8, 2001).

K. Bhattacharya and J. Li, "Domain patterns, texture and macroscopic electro-mechanical behavior of ferroelectrics", To appear in 2001 *Workshop on Fundamental Physics of Ferroelectrics* (ed. H. Krakauer), AIP, 2001.

Y.C. Shu and K. Bhattacharya, "Domain patterns and macroscopic behavior of ferroelectric materials", *Philosophical Magazine* 81 2021-2054, 2001.

E. Burcsu, G. Ravichandran, K. Bhattacharya, "Observation of Domain Motion in Single-Crystal Barium Titanate Under Combined Electromechanical Loading Conditions", In *Proceedings of the IUTAM Symposium on Mechanics of Martensitic Phase Transformations in Solids, Hong Kong, June 2001* (ed.Q.P. Sun), 2002.

J. Li and K. Bhattacharya, "A mesoscale electromechanical theory of ferroelectric films and ceramics", In *2002 Workshop on Fundamental Physics of Ferroelectrics* (ed. R.E. Cohen).

E. Burcsu, G. Ravichandran, K. Bhattacharya, "Experimental studies of the large strain electrostrictive actuation in barium titanate", *Journal for the Mechanics and Physics of Solids.* To appear, 2003.

K. Bhattacharya and G. Ravichandran, "Ferroelectric perovskites for electromechanical actuation", *Acta Materialia.* To appear, 2003. Invited review for the 50th anniversary issue of *Acta Materialia.*

J. Li and K. Bhattacharya, "The effective electromechanical behavior of polycrystalline ferroelectric ceramics and films", *Archive for Rational Mechanics and Analysis.* In preparation.

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J. Li and K. Bhattacharya, "Electromechanical Behavior of Polycrystalline Ferroelectrics: Crystallography and Texture", *Physical Review Letters*. In preparation.

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(3) Report of Inventions
None

(4) Scientific Progress and Accomplishments

Ferroelectric materials are currently used in a variety of sensor and actuator applications. Conventional materials offer a high frequency, linear response with useful strains of up to 0.1%. Additional applications can be imagined for actuators that generate a greater degree of strain. The current investigation is aimed at offering increased actuator performance over conventional materials. In addition, the study offers insight into the underlying principles of behavior of those materials currently in use. Experimental studies of large strain actuation has been carried out using a single crystal in a novel configuration, and theoretical studies have explored the possibility of extending this idea to polycrystals and to the ferroelectric-antiferroelectric phase transformation.

Experimental Studies

The basic principle of operation for large strain actuation using a ferroelectric single crystal is illustrated in figure 1. A thin single crystal plate, is subjected to a constant, uniaxial compressive stress (P) and a variable electric field. At zero applied voltage, the applied stress forces the polarization to be in-plane, as illustrated in the figure. As the voltage is increased, the electric field tries to align the polarization in the out-of-plane direction, but this is resisted by the stress. There is an exchange of stability at a critical voltage and the polarization switches with an accompanied strain. Finally as the voltage is decreased, the polarization reverts back to an in-plane direction, recovering the strain. Thus, as the load is held fixed and the voltage cycled, domain switching provides an electrostriction as large as 1.1%. Strains as large as 6% are predicted for other materials of the same class.

An experimental setup was designed to demonstrate the principle of large electrostriction in single crystal ferroelectrics through combined electromechanical loading and to further study the behavior of these materials under the combined loading conditions. The setup consists of a loading mechanism, displacement measurement transducer, high-voltage power supply and long

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working distance video microscope. The system was designed to apply a constant compressive load and variable electric field to a ferroelectric crystal. It was further designed to allow accurate measurement of strain and polarization, as well as allow real time *in situ* observation of the domain patterns during the experiment.

Experiments were performed on single crystals of barium titanate of (001) and (100) orientation at various levels of stress. During the experiment, a slow voltage signal is generated and the strain and polarization are measured. A series of strain-electric field trajectories are shown in figure 2 at six values of compressive stress. The data are from the fifth cycle of each experiment for an initially (001) oriented crystal. The first plot has a compressive stress of approximately zero (there is a small stress present due to the measurement method). In this case, the total strain is less than 0.1 %. With subsequent increase in compressive stress, there is an increase in the maximum strain up to 0.9 % at 2.14 MPa, and a broadening of the butterfly hysteresis loops. As the stress is further increased, the maximum strain decreases as the applied field is not able to overcome the applied stress. Figure 3 shows a series of polarization-electric field trajectories for the same cases. For the zero stress case, the hysteresis curve has very sharp corners as is usually observed for single crystal ferroelectrics. As the stress is increased, there is a blunting of the corners.

The steady state actuation strain as a function of compressive stress is summarized in figure 4. The actuation strain is defined as the difference between the maximum and minimum strain for a given half cycle and was calculated in the fifth cycle of each experiment. Data for initially (100) and (001) oriented crystals are shown. There is a clear increase in actuation strain with increasing stress in each case. This actuation strain reaches a maximum level and then begins to decrease. Coercive field, defined as the field required to reduce the polarization to zero, is shown as a function of compressive stress in figure 5. The coercive field is found to be relatively insensitive to stress with an increase of about 20-30 V/cm/MPa. The use of in situ microscopy yields images of the domain structure such as those in figure 6. Further work is being done to correlate the observations from the images to the crystal averaged values of strain and polarization.

Theoretical Studies: Polycrystals

Theoretical studies have examined whether this mode of large strain actuation could be extended to polycrystalline ceramics, and if so what textures would be required to maximize the actuation. Additionally, the theoretical studies have addressed the widely known, but incompletely understood , observation that Lead Zirconate Titanate (PZT) is easier to pole at compositions close to the morphotropic phase boundary.

A detailed model of the effective electromechanical properties of ferroelectric crystals that includes implicitly the domain patterns and the polycrystalline texture has been developed. It starts with a Landau-Ginzburg type model adapted to heterogeneous materials, and finds the large scale behavior using the framework of relaxation and homogenization assuming separation of scales between the macroscopic specimen, grains and domains. The important ideas are illustrated in Figure 7. The set of possible effective remnant polarizations and strains of single crystals with multiple domains is characterized for various crystal systems. The set of possible effective remnant polarizations and strains of polycrystalline ceramics is also characterized and evaluated for different materials and textures using the Taylor bound.

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It is established that a polycrystal of a material which is cubic above Curie temperature and <100> polarized tetragonal below has no remnant polarization or strain unless it has a strong <100> texture. Similarly, a polycrystal of a material which is cubic above Curie temperature and <111> polarized rhombohedral below has no remnant polarization or strain unless it has a strong <111> texture. Thus, it is necessary to use highly textured single crystals to obtain large strain actuation in ceramics of these two classes of materials. In stark contrast, a polycrystal of a material which is cubic above Curie temperature and <11w> polarized monoclinic always has some remnant polarization and strain irrespective of texture, though there are special textures for which it is maximized.

These observations also explain the better polability of Lead Zirconate Titanate (PZT) near the morphotropic phase boundary. Titanium rich PZT is tetragonal, while Zirconium rich Titanate is rhombohedral, but PZT is monoclinic at the morphotropic phase boundary.

Theoretical Studies: Ferroelectric-antiferroelectric transformation

During the final year, the attention focussed on ferroelectric-antiferroelectric transformation. We discuss the specific case of lead-zirconate ($PbZrO_3$) to explain the ideas. Pure lead-zirconate ($PbZrO_3$) undergoes a phase transformation from a cubic non-polar perovskite state at high-temperature to a tetragonally distorted anti-ferroelectric state[1] (AFE) at low temperature. When subjected to an electric field along a pseudo-cubic axis at low temperature, it undergoes a further phase transformation from the tetragonally distorted AFE to a rhombohedrally distorted ferroelectric state[2] (FE). This is the so-called ferroelectric- antiferroelectric phase transformation. The temperature vs. electric field phase diagram is shown schematically in Figure 8.

This AFE-FE phase transformation potentially offers very interesting possibilities for actuation. If we take a $PbZrO_3$ crystal at room temperature and subject it to an cyclic electric field along a pseudocubic direction (schematically indicated by the dashed line in Figure 8), the crystal switches cyclically and reversibly between the AFE and FE states. This switching is accompanied with a large distorsion, which can be exploited as large actuation strain. Note in particular, that there is no need to apply the mechanical loads to obtain reversal as we had to do in $BaTiO_3$.

We undertook a theoretical study to understand if this potential could be exploited in practice for large strain actuation. The key issue is to understand the energy barriers for such a transition and to design a configuration that maximal actuation. This requires us to develop a model that is detailed enough to study the domain patterns, but at the same time tractable enough to study macroscopic specimens. A purely atomistic theory would not be able to deal with macroscopic bodies, and a macroscopic atomistic continuum theory will not be able to deal with details of the

[1] An anti-ferroelectric material is one where the crystal lattice is spontaneously polarized at a molecular scale, but the polarization alternates between opposite directions so that there is no macroscopic polarization.

[2] A ferroelectric material is one where the crystal lattice is spontaneously polarized at both the microscopic and macroscopic states.

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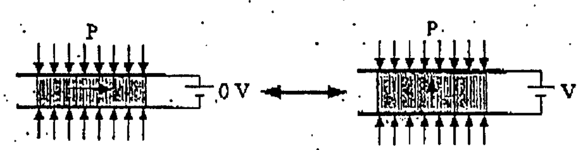
domains. Therefore we chose to proceed along the lines of Shu and Bhattacharya[3]. Their model and theoretical investigation motivated the successful experiments on $BaTiO_3$ that were reported during the previous years. Therefore, it was natural to extend the Shu-Bhattacharya model to anti-ferroelectrics.

The key idea of this model is to introduce a "meso"-scale between the atomistic (micro-scale) and the continuum (macro-scale). The meso-scale is the scale on which the polarizations are almost constant so that it represents the scale of domains. Specifically, at this scale the polarization is non-zero is a FE while it is non-zero in an AFE. We then introduce an energy functional at this meso-scale. It is important that this meso-scale energy correctly represents the underlying physics at the micro-scale. In particular, it is crucial and difficult to understand the non-local (dipole-dipole interaction) energy of the polarizations since they can oscillate at the micro-scale in an AFE. We accomplished this step using a coarse-graining (micro to meso passage) using a method first proposed by James and Müller[4] in the context of magnetism. We showed that the non-local dipole-dipole interaction at the micro-scale manifests itself completely locally in an AFE but non-locally in a FE. We finally used energy wells to capture the spontaneous polarization and distorsions.

We used the energy functional to study the behavior at the meso-scale (domain patterns) and its influence on the macroscopic behavior of the material during the AFE-FE transition. In particular we studied all possible interfaces between the FE and AFE states. An important result is that there is no low energy interface between a homogeneous AFE and homogeneous FE states[5]. Instead all interfaces would require either the FE or the AFE states to be frustrated. This in turn means that either the AFE-FE transformation will yield very little strain or will require large electric fields. We conclude therefore that the AFE-FE transformation, despite all its attractive features is not feasible for large strain actuation. This will not be pursued further.

While the application to actuation is disappointing, it is a demonstration of modeling that guides experiments and design. Further, the model we have developed will find a variety of uses in other applications which we plan to pursue in the future.



[3] Y.C. Shu and K. Bhattacharya, "Domain patterns and macroscopic behavior of ferroelectric materials", Philosophical Magazine **81** 2021-2054, 2001.

[4] R.D. James and S. Müller, "Internal variables and fine-scale oscillations in micromagnetics", Continuum Mechanics and Thermodynamics 6 291-336, 1994.

[5] Unless the spontaneous polarization and distortions satisfy some highly non-generic conditions.

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Figure 1 – Mode of operation for large strain electrostriction in a ferroelectric single crystal.

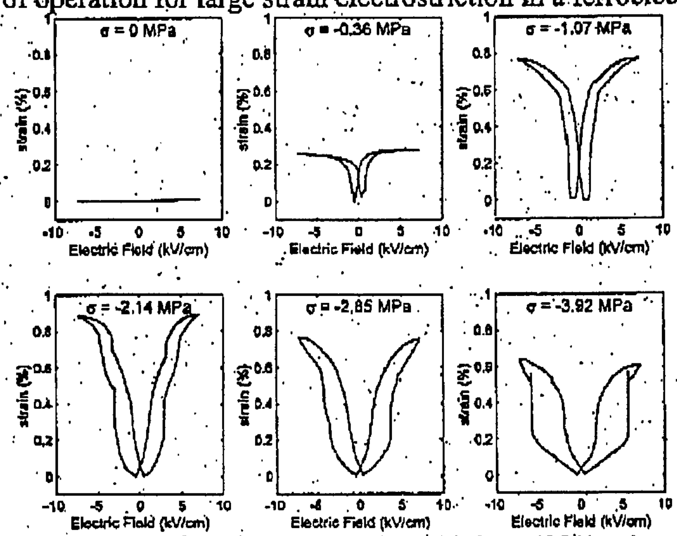

Figure 2 – Strain response as a function of electric field for a (001) oriented barium titanate crystal at different levels of compressive stress.

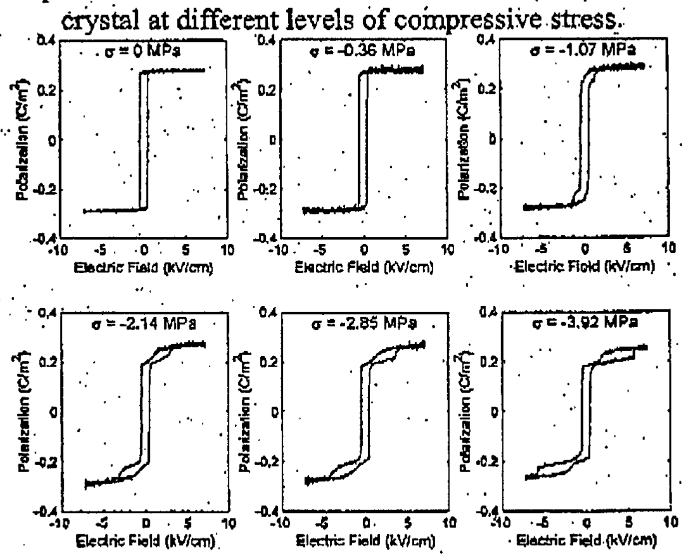

Figure 3 – Polarization as a function of electric field for a (001) oriented barium titanate crystal at different levels of compressive stress.

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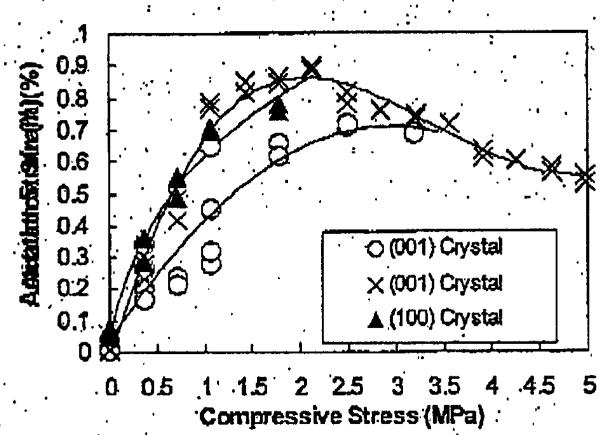

Figure 4 – Steady state actuation strain vs. compressive stress for barium titanate crystals.

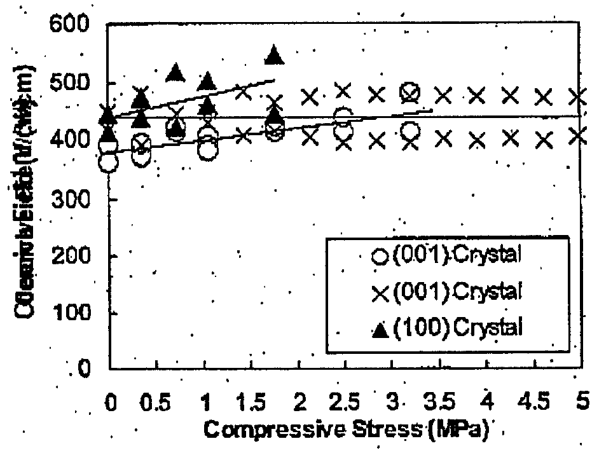

Figure 5 – Coercive field vs. compressive stress for barium titanate crystals.

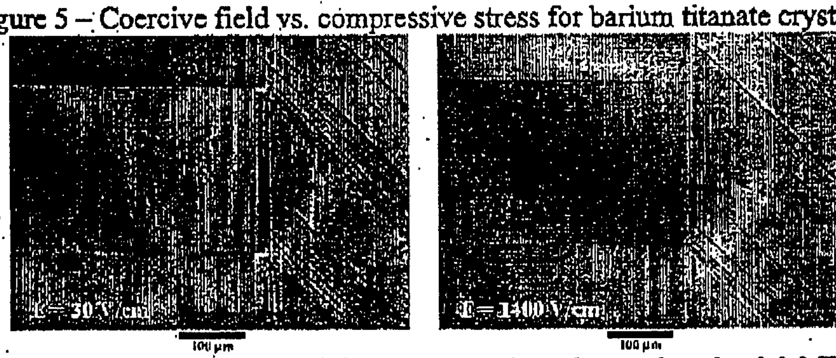

Figure 6 –Images of domain pattern in initially (001) oriented crystal under 3.2 MPa compressive stress at an electric field of 30 V/cm 1400 V/cm.

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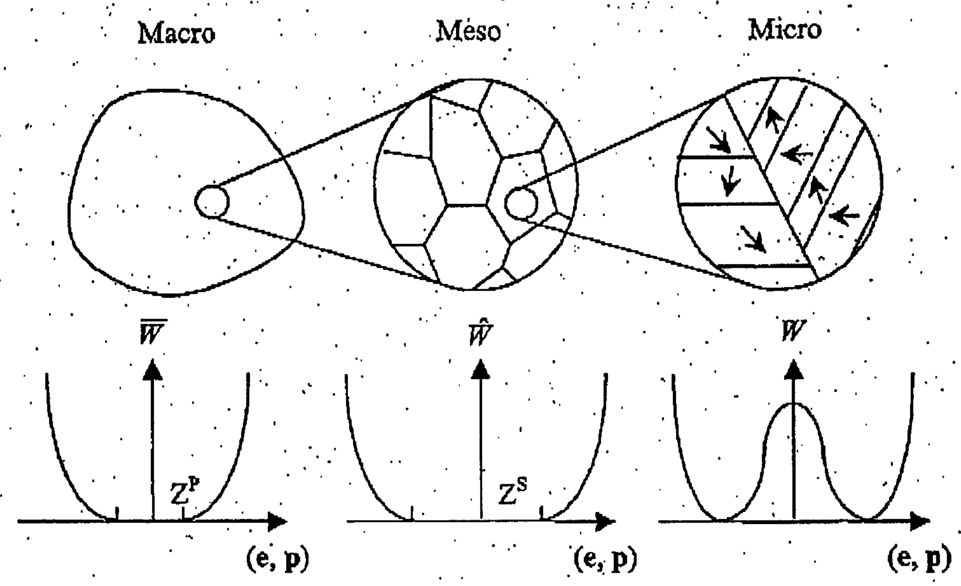

Figure 7 - The multi-well structure of stored energy density W, the effective energy density of a single crystal $\hat{W}$, and the effective energy density of a polycrystal $\overline{W}$.

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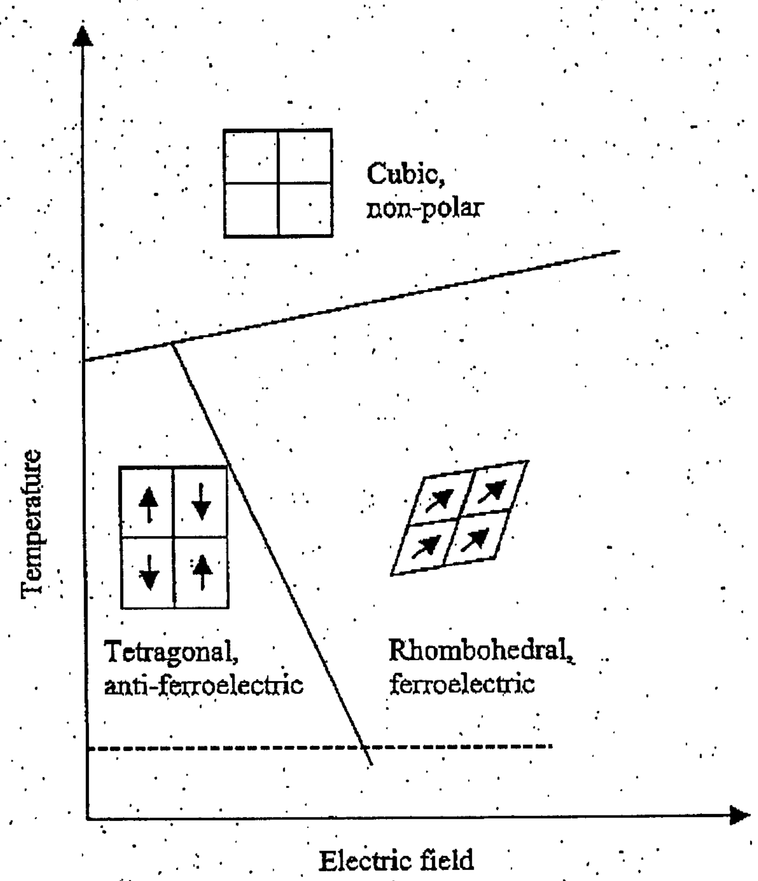

Figure 8: The temperature vs. electric field phase diagram for Lead Zirconate ($PbZrO_3$)